

SCIENCE FOR GLASS PRODUCTION

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CERTAIN PARTICULARITIES OF TRANSPORT PHENOMENA IN GLASSMAKING FURNACES

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The general principles and particularities of transport phenomena in glass-forming melts and glassmaking furnaces are examined. It is shown that the transport phenomena are associated with physical–chemical factors and that the thermodiffusion phenomena play a role in the formation of the colored layers of molten glass. It is noted that to obtain high product quality it is important to follow the process regimes strictly.

Key words: transport phenomena, thermodiffusion, glassmaking furnace, coloration, uniformity.

It is well known that transport phenomena incorporate processes in which mass or energy is transferred from some parts of a nonuniform material system to other parts. Ordinarily, a system is assumed to consist of a single phase but have nonuniform properties. The most important types of transport are the transport of impulse or momentum (viscous flow), heat (heat conduction), mass (diffusion), and electrical energy (charge transfer in an electric field). The transport phenomena are similar to one another and intercoupled. Also, there is an analogy between the transport mechanisms for particles and those for impulse or momentum, which determine the resistance to particle motion (momentum — the product of mass and velocity — mv ; impulse of force — the product of force and time — $F\tau$; the impulse of a force equals the momentum change: $F\tau = \Delta mv$). The existence of this condition determines the resistance arising in gas or liquid media to motion as a result of viscosity. The balances of the transport phenomena in thin layers of gas and condensed media are presented in Diagram 1.

The study of transport phenomena in multicomponent melts is important from the standpoints of theory and applications. It should be noted that in the event of mass transport occurring together with ordinary diffusion due to a concentration gradient both thermo- and barodiffusion occur; they characterize diffusion phenomena in gaseous and condensed media in the presence of temperature and pressure gradients. If these latter gradients are constant, then a concentration

gradient arises in the interior volume of the system, giving rise to ordinary diffusion also.

At the same time, thermo- and barodiffusion phenomena are studied mainly for gases and dilute solutions. Barodiffusion arises only at very high pressures; it may be neglected for processes occurring at atmospheric or comparatively low pressure. Thermo- and barodiffusion are non-negligible only in geochemical and geophysical processes, the formation of oceanic flows, physical – chemical interactions in soils, and so forth.

Some technological processes are based on thermodiffusion. Thermodiffusion phenomena must be taken into ac-

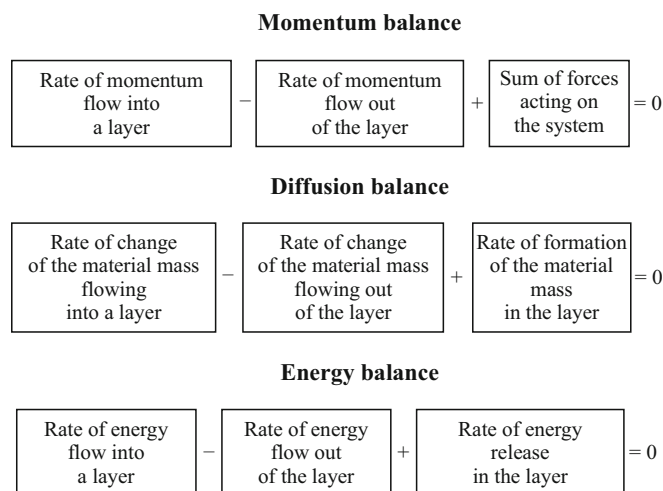


Diagram 1.

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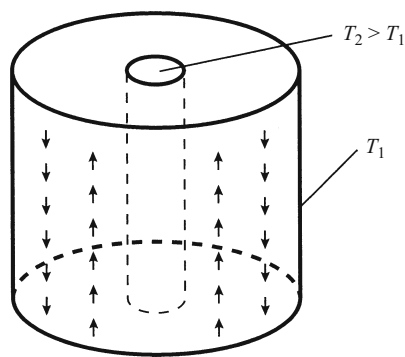


Fig. 1. Schematic diagram of an apparatus for separating isotopes.

count in certain technological processes, including in glass production. The most famous technological process based on thermodiffusion is isotope separation (Fig. 1).

The apparatus for separating isotopes consists of two coaxial tubes (with different temperatures) between which a gas is present. The temperature difference creates vertical convective flows of the gas mixture or solution and simultaneously generates continual transverse thermodiffusion separation of isotopes. As a result, the lighter isotopes accumulate on the hot surface of the inner tube and move upwards while the heavier isotopes accumulate on the cold surface of the outer tube and move downwards. Such columns operate most efficiently with gas mixtures because the diffusion resistances are smaller. Ordinarily, multicycle systems are used because the separation factor is quite small. Thermodiffusion in solutions is called the Sorét effect, after the name of the Swiss chemist Ch. Sorét who was the first to investigate thermodiffusion (1879 – 1881).

The total diffusion flux in a binary mixture at constant pressure with no external forces is

$$J_i = -nD_{1,2} \text{grad } c_i - n(D_T/T) \text{grad } T,$$

where $D_{1,2}$ is the diffusion coefficient (concentration diffusion); n is the number of particles per unit volume of the mixture; D_T is the thermodiffusion coefficient; $c_i = n_i/n$ is the particle concentration of the i th component ($i = 1, 2$); and, T is the temperature.

The concentration distribution in the stationary state can be found from the conditions $J_i = 0$, whence

$$\text{grad } c_i = -(k_T/T) \text{grad } T,$$

where $k_T = D_T/D_{1,2}$ is the thermodiffusion ratio, which is proportional to the product of the component concentrations.

The equations for multicomponent systems are much more complicated. The theoretical principles of thermo- and barodiffusion are quite complex and have not been adequately developed, especially for condensed media. Some assumptions are examined in [1 – 3]. The acquisition of experimental data on the thermodiffusion coefficients is fraught with the difficulties of taking account concentration diffusion

counterflows, even for inviscid liquids. H. Wessels presents in his work (1914) only approximate values: $D_{1,2} \approx 10^{-9}$ and $D_T \approx 10^{-11}$ m²/sec. In this case the thermodiffusion ratio is $k_T \approx 10^{-2}$. The first experiments on thermodiffusion using cobalt-colored boron glasses were performed strictly. After a holding period of many days (10 – 20 days) in the presence of a definite temperature gradient, only a negligible shift of the coloration maximum — 3 – 4 mm — was observed. In this case the following relation can be used to determine the thermodiffusion coefficient approximately:

$$x^2 = D_T \tau,$$

where x is the thickness of the layer of high coloration intensity, m; D_T is the thermodiffusion coefficient, m²/sec; and, τ is the time, sec.

Calculations using this relation give $D_T \approx 10^{-12}$ m²/sec.

Transfer phenomena play an important role in the technological processes involved in the production of glass and glass articles — starting with the process of making glass and ending with treatment processes and interaction with the environment once the glass articles are in use [4, 5]. For example, thermodiffusion phenomena associated with the mass transfer of gases in solid glass are observed when electrovacuum and gas-discharge apparatus is in use [6].

Transport phenomena have not been adequately studied for complicated physical – chemical processes in glass-making furnaces; thermo- and barodiffusion phenomena have not been studied at all. The reason is that considerable methodological difficulties arise in working with high-temperature viscous glass-forming, especially, silicate, systems.

In the production of mass-produced articles (sheet glass, glass containers, dishware) the molten glass is not have an entirely uniform chemical composition or temperature. This concerns especially any molten glass that is made in continuous-flow glassmaking furnaces with high output, which is characteristic for the furnaces used in the production of glass containers. Under these conditions, when contact occurs with nonuniform sections or the molten glass comes into contact with refractory materials temperature gradients affect mass-transfer phenomena directly or indirectly.

Certain features of the transport phenomena occurring in a molten glass are examined below.

Diffusion in Silicate Melts. In melts, as in solids, the main form of motion of the particles is oscillation around positions of equilibrium, though the latter are not strictly fixed. It can be assumed that the particles move along interstices with the position of the sites themselves changing continually. Different ions have different mobility in the melt; each ion moves much more rapidly in the liquid than in the solid phase.

The following factors affect the rate of motion (diffusion) of ions in a melt:

the strength of the cation – oxygen bond; the stronger this bond, the less mobile the ion;

the melt density; the more dense the melt structure, the lower the diffusion rate, since a moving ion must overcome a stronger counteraction when other ions and melt fragments are in close proximity;

the ion size; the larger its radius, the more slowly an ion moves in a dense melt.

The nature of the melt determined the effect of these factors. For example, the density plays only a small role in melts with an open structure; the cation – anion bond strength has a greater effect. However, the density and size factor assume a decisive role in dense melts. It should be noted that this effect is characteristic for binary melts; it becomes more complicated in multicomponent melts, but the effect of these factors remains.

Motion of the Molten Glass in Industrial Furnaces and Diffusion Phenomena. All basic processes in glass-making furnaces occur with the participation of diffusion phenomena: the interaction of the components during the founding process, dissolution of SiO_2 in the glass-forming melt, interaction of refractories and molten glass, convective motion of the molten glass in the furnace. Under certain conditions these phenomena can produce a macroscopic change in the uniformity of the system, giving rise to, together with a useful effect, undesirable consequences in the course of the production process [4, 5, 7].

Transfer phenomena, especially diffusion phenomena, in fused glass are of a distinctly kinetic character because of the high viscosity of the melts. For diffusion phenomena, this means that their duration is very considerable and the results manifest over longed time intervals.

Glassmaking furnaces are operated over long periods of time. For a prescribed glass composition, a more or less constant temperature distribution over the depth of the pool and convective flows are established in the molten glass. Figure 2 displays a scheme of the convective flows and the temperature distribution in the surface and bottom layers of the molten glass for a furnace which is used to make container glass. The temperature gradients and the process flow determine the character of the convective motion of molten glass in a furnace. Ordinarily, a stationary layer of molten glass, which can reach 50 mm in thickness depending on the type glass and the constancy of its composition, the stability of the temperature regime, and a number of other factors, forms at the bottom of the furnace. This bottom layer is formed as a result of heat losses through the bottom of the furnace (this layer is somewhat thinner in furnaces with a “warm” bottom) and because radiative heat transfer is weakened as a result of heat absorption over the depth of the pool.

Any study of diffusion phenomena in high-viscosity melts of glassmaking furnaces must take account of three interaction regions [2 – 4]:

the main volume of the melt, where the concentration of the diffusing material is negligible compared with the saturation concentration; molten-glass motion in this volume is due to process and convective flows;

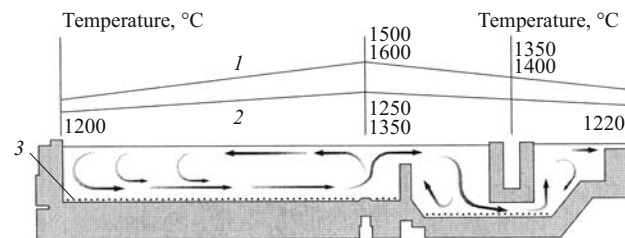


Fig. 2. Diagram of molten glass flows and temperature profiles in a glassmaking furnace for the production of container glass: 1) layers close to the surface; 2) layers close to the bottom; 3) molten-glass – refractory contact layer at the boundary.

a region where concentration distribution is constant and convective diffusion occurs at a certain distance from the interaction surface — the hydrodynamic boundary layer; laminar flow occurs here and the viscosity of the melt plays the main role; for diffusion phenomena, relatively thick boundary layers are formed in fused glasses and other silicate melts, which are high-viscosity slow-moving liquids;

a region directly adjoining the interaction surface — the diffusion layer — where the ion concentration changes rapidly and ion diffusion occurs; saturation concentrations are reached here; for example, when the molten glass interacts with a refractory material this layer adjoins the surface of the refractory; the diffusing particles are transported from here into the melt by convective diffusion through the hydrodynamic boundary layer; the thickness δ_D of the diffusion layer is very small and can be approximately determined from the relation

$$\delta_D = \delta / \text{Pr}^{1/3},$$

where δ is the thickness of the hydrodynamic layer and Pr is the diffusion Prandtl number.

It follows from this relation that the thickness of the diffusion layer decreases considerably with increasing viscosity of the liquid.

Physical – Chemical Interactions. As a rule, all transfer phenomena are intercoupled. At the same time, mass transfer in molten glass can give rise to physical – chemical interactions which are associated with, for example, the formation of coloration complexes. The most characteristic example is the interaction of the iron and sulfur ions in ready molten mass, resulting in the formation of amber chromophore complexes.

It is well known that when Na_2SO_4 is used for fining glass and substituting for calcined soda, under certain conditions sulfur exists in the forms S^{6+} (SO_4^{2-} or SO_3), S^{4+} (SO_2), and S^{2-} . It is also possible that S^0 nanoparticles exist as an intermediate state. As a rule, SO_4^{2-} ions predominate in oxidized glass and the content of S^{2-} ions increases appreciably in reduced glass; the latter ions produce the amber and brown colors of glass with varying intensities.

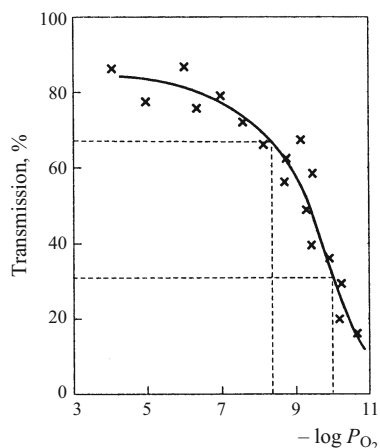
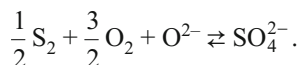
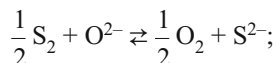


Fig. 3. Transmission of glass at wavelength 550 nm as a function of the reducing potential of the medium.

The redox equilibria of iron oxides and the solubility of sulfur in glass melt, depending on the oxygen partial pressure and other factors, are reflected in the investigations performed by S. Fincham and F. Richardson (1954), W. Johnston (1964), S. Buda (1965), S. Holmquist (1966), W. Manring, et al. (1967), and H. Williams (1978). The results of these and other investigations are summarized in [4, 7].

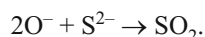
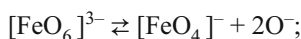
According to the data obtained by S. Fincham and F. Richardson, the solubility of sulfur in glass melts can be represented by two redox equilibria:



In accordance with these equations, it was established that the SO_4^{2-} concentration is directly proportional to and the S^{2-} concentration inversely proportional to the oxygen partial pressure.

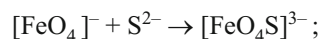
Conditions under which an amber chromophore forms and its concentration increases as well as the conditions under which dark brown color and fine bubbles form are created in a stationary contact layer at the boundary with refractories [4, 7].

The conditions for the formation of an amber chromophore are shown in Fig. 3 as function of the oxygen partial pressure. In this connection, the oxygen partial pressure at the locations of amber chromophore formation can reach $10^{-8.5} - 10^{-10}$ MPa and less. Unstable reactive complexes $[FeO_4]^-$ and S^{2-} form in the melt under these conditions. As a result of S^{2-} ions being present in the melt, the oxygen ligands become bound into SO_2 molecules. Fine bubbles can appear:



Subsequently, the reaction forming the amber chromophore proceeds according to the following ligand substitution mechanism:

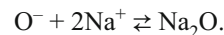
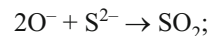
formation of an intermediate compound (or, simply, intermediate) with a large coordination number:



restructuring of the intermediate by means of "matched" movement of the ligands:



The Na^+ or Ca^{2+} ions neutralize the excess charge of the amber chromophoric complex. The detached oxygen ligands interact with the S^{2-} and Na^+ ions present in the melt, forming SO_2 molecules and cationic structural fragments:



Some Particularities of Diffusion Phenomena in Glassmaking Furnaces. As noted above (Fig. 2), quite substantial temperature gradients over the pool depth are observed in furnaces used for making container glass. As a result, stratified thermodiffusion phenomena will be observed. As a result of these phenomena, because of the temperature difference the light sodium ions will diffuse into the more heated layers and the heavier aluminum, iron, selenium, and other ions will diffuse into the less heated layers. The lower the layer is in the molten glass pool, the more enriched with heavy ions the layer is. Some diffusing ions migrate into the convective flows, from which some ions, especially the light ions, migrate into the production flow and some heavy ions migrate into the bottom layers.

As a result of the long operating period of glass-making furnaces (several years), differentiation of the chemical composition of the molten glass over the depth of the pool in the glassmaking furnace occurs gradually, including by means of thermodiffusion. This has been confirmed during cold maintenance work performed on glassmaking furnaces. Examinations of a number of furnaces after shutdown for cold maintenance have shown that the pattern of differentiation of the molten glass over the depth of the pool for different glass compositions and types of furnaces is different with respect to composition and color hues. As a rule, Fe_2O_3 , FeO , Al_2O_3 , and Se compositions increase over the depth of the glass mass, and the ratio of different degrees of oxidation of the sulfur changes.

The colorless glass mass remaining in the furnace pool exhibits different color hues, which are especially noticeable when the thickness of the layer is considerable and range from colorless to grey and sometimes rose (with excess physical bleaching agent — selenium). The glass in the contact layer immediately adjoining the refractories on the furnace bottom can be greenish-blue and brown with different

intensities. For green glasses, colored by Cr_2O_3 , the color becomes darker over the pool depth. This darkening is due to an increase in the content of iron oxides. A brown tinge and fine bubbles are observed in the bottom layers and in the contact layer at the boundary with the refractories. It should be noted that, of course, there are no sharp boundaries between the layers with different color hues; this shows that diffusion counterflows and convective motion of the molten glass occur, though these motions are very slow.

In furnaces used for the production of colorless container glass, the temperature gradient between the surface and bottom layers is $200 - 250^\circ\text{C}$. For colored glass, this gradient can reach 350°C . Conditions for directed, though negligible, thermodiffusion flow are created in these cases; this flow is complicated by convective motion of the molten glass and production of the glass articles as well as by the concentration-driven counterdiffusion.

Nonetheless, a definite differentiation of the melt with respect to the composition and color hues occurs when the factors indicated above operate for a long time (of the order of several months). Gradual enrichment of the low-lying layers of the molten glass with heavy iron, chromium, and selenium ions together with a decrease of the oxygen partial pressure intensifies the processes with reduced forms of the indicated ions and sulfur being formed [4, 7]. It is known that under reducing conditions very small amounts of iron and sulfur ions are needed to form an amber chromophore [8]. Therefore, transport phenomena, including thermodiffusion, can create the conditions required for amber chromophore to form via the mechanism described above.

When making colorless container glasses, attention must be paid to the purity of the raw materials used not only with respect to iron oxides but also with respect to organic impurities. Thus, when too little clean cullet is used, for example, cullet with plastic caps on the neck, the molten glass produced can have a yellow hue due to the decomposition of organic substances, creation of local reducing conditions, and formation of an amber chromophore.

The molten glass made in continuous-flow glassmaking furnaces with sufficiently high specific output is not very

uniform. High stability of the process regimes is very important for such furnaces in order to avoid scrap. As a result of temperature fluctuations during the production of colorless and colored glasses, deep nonuniform sections of the molten glass can enter the process flow. Ordinarily, articles are formed from nonuniform portions of the molten glass because of the appearance of defects in the form of splits, a nonuniform distribution of the glass, and inadequate thermal and mechanical strength.

Modern glassmaking furnaces for the production of glass containers are highly efficient (high output of molten glass with relatively low specific heat consumption). The pouring sill, the deep fining zone (deep refiner), relatively process output channel with effective cooling of the molten glass (see Fig. 2) together with strict adherence to the process regimes can completely eliminate the appearance of critical situations. But, nonetheless, the molten glass in the pool shows definite differentiation due to the particularities of the transport phenomena in glass melts. This must be taken into account in the production process to ensure high product quality and to avoid scrap.

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